

One-step model of photoemission for non-local potentials

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The one-step model of valence-band photoemission and inverse photoemission from single-crystal surfaces is reformulated for generalized (non-local, complex and energy-dependent) potentials. Thereby, it becomes possible to account for self-energy corrections taken from many-body electronic-structure calculations. The original formulation due to Pendry and co-workers employs the KKR multiple-scattering theory for the calculation of the initial state. This prevents a straightforward generalization of the one-step model to non-local potentials. We therefore consider the Dyson equation which is set up within a muffin-tin-orbitals representation as an alternative to obtain the initial-state Green function. This approach requires a revision of the transition-matrix elements which is carried out in detail. The final state is considered as a time-reversed LEED state as usual. The proposed generalization of the one-step model allows to distinguish between the bare photocurrent reflecting the (quasi-particle) band structure and the secondary effects due to the (dipole) selection rules and due to the wave-vector and energy dependence of the transition-matrix elements.

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I. INTRODUCTION

Much information on the electronic structure at crystal surfaces is gained by ultraviolet photoemission spectroscopy (PES) [1–5] and inverse photoemission spectroscopy (IPE) [6–10]. Energy- and angle-resolved PES and IPE are useful tools for analyzing the dispersion of (quasi-particle) bands. For the sometimes rather involved interpretation of measured spectra, a comparison with theoretical results for the electronic structure is inevitable. However, measured energy- and angle-resolved spectra can hardly be compared with the calculated band structure directly: Secondary effects due to the wave-vector and energy dependence of the transition-matrix elements and due to selection rules considerably distort the “bare” spectra. Even if the primary interest rests on the bare quantities, such as the density of states and the dispersion of bands, a theory of photoemission is needed to build the bridge between the photoemission experiments and the electronic-structure calculation.

The so-called one-step model of photoemission has quite successfully fulfilled this demand in recent years. The original method as proposed by Pendry and co-workers [11–13] has been the starting point for several generalizations and improvements, which became necessary as the experimental technique was more and more refined and growing interest was spent on more complex materials. Inverse photoemission in connection with a realistic model for the surface barrier [14,15,8] has enlarged the applicability of the one-step model. The relativistic generalization [16–20] made possible investigations of spin-polarized photoemission from non-magnetic materials [21,22]. The extension of the one-step model to magnetic materials resulted in theoretical studies of the magnetic circular and linear dichroism [23,24]. Photoemission from covalently bonded systems, adsorbate-covered surfaces and from materials with a relatively open crystal structure brought the need to overcome the muffin-tin potential model on which the original one-step formulation was based. The generalization of photoemission theory with respect to space-filling potentials [25,26] and the development of a relativistic, full-potential one-step model for materials with several atoms per unit cell [27] has more or less completed recent work on that matter.

The one-step model of (inverse) photoemission starts from a given electronic potential which is needed for the necessary construction of multiple-scattering states and propagators. This potential is taken from a separate electronic-structure calculation and must be considered as the decisive input for the one-step model: The peak positions in the calculated (inverse) photoemission spectrum directly reflect the energetics of the electronic structure that evolves from the potential given. The reliability of the PES (IPE) theory is thus intimately related to the “quality” of the potential for the system at hand.

The one-step model has been originally formulated for a *local* potential $V(\mathbf{r})$. A local potential is provided by density-functional theory (DFT) within the local-density approximation (LDA) [28–33]. In practice, such LDA inputs for photoemission calculations have been proven to yield rather satisfactory results when compared with experimental spectra from several materials [34–36]. The use of LDA potentials has thus become a well-known and widely used concept in the photoemission theory.

On the other hand, when applying the theory to strongly correlated electron systems,

it surely becomes doubtful whether this concept is still adequate since implicitly the LDA eigenenergies are interpreted as to be the one-particle excitation energies of the system. It is well known that there are two possible sources of error connected with that interpretation: Firstly, the LDA only provides an approximate expression for the (local) exchange-correlation potential. Secondly, even with the exact exchange-correlation potential at hand, one is left with the problem that there is no known correspondence between the Kohn-Sham eigenenergies and the one-particle excitation energies [33,37–39].

For an in principle correct description of the excitation energies the non-local self-energy has to be considered. This, however, constitutes a many-body problem. Therefore, DFT-LDA calculations must be supplemented by many-body methods to arrive at a realistic description of the one-particle excitations in strongly correlated systems. To give an example, let us mention the GW approximation [40] which is well suited for the case of insulators and semi-conductors but has also been applied successfully to transition metals [40–43]. Another approach is to consider Hubbard-type models where those Coulomb-interaction terms are included explicitly that are assumed to be treated insufficiently within DFT-LDA. As some recent studies of this type show, significant improvement upon the LDA predictions for transition metals is possible indeed [44–51].

The self-consistent potential $U(\mathbf{r}, \mathbf{r}', E)$ resulting from the GW approach, consists of a local part $V(\mathbf{r})$ which can be identified with the LDA potential and of the non-local self-energy $\Sigma(\mathbf{r}, \mathbf{r}', E)$ which is energy-dependent and complex. A tight-binding one-particle basis is used by those approaches that start from (multi-band) Hubbard-type models. Consequently, the resulting generalized potential is given in the form $U_{ii'}^{LL'}(E)$ where i refers to sites, and L is an orbital quantum number. Again, U can be decomposed into a term $V_{ii'}^{LL'}$ resulting from the local one-particle potential in the Hamiltonian, and into the self-energy $\Sigma_{ii'}^{LL'}(E)$ resulting from the interactions. Note that transformation to the real-space representation yields a non-local self-energy $\Sigma(\mathbf{r}, \mathbf{r}', E)$, even if it is local in the tight-binding basis, $\Sigma_{ii'}^{LL'}(E) \sim \delta_{ii'}$.

As concerns a theory of PES and IPE, we have to face the following problem: Strong electron correlations imply the need for self-energy corrections to obtain a realistic description of the elementary excitations. Consequently, a generalized potential should be considered to be the starting point for the actual (inverse) photoemission theory. The non-locality of the potential, however, causes difficulties within the original formulation of the one-step model: The calculation [12] of the one-electron initial-state Green function $G(\mathbf{r}, \mathbf{r}', E)$, which is directly related to the (bare) photocurrent as well as the subsequent evaluation of the matrix elements is based on the Korringa-Kohn-Rostocker (KKR) multiple-scattering approach [52,53] and is thus intrinsically limited to the case of local potentials. This seems to prevent a straightforward generalization of the theory to non-local potentials and thereby an application to strongly correlated systems.

The purpose of the present paper is to demonstrate that it is possible to overcome the mentioned restriction. Starting from Pendry's formula for the photocurrent [12], we propose a reformulation of the one-step model such that a general (non-local, complex, energy-dependent) potential $U(\mathbf{r}, \mathbf{r}', E)$ can be included via the Dyson equation in the calculation of the initial-state Green function. For the final state the usual (layer-KKR) multiple-

scattering theory [52–55,11] is retained. Our approach requires a complete revision of the transition-matrix elements. This is carried out in detail. Compared with earlier theoretical approaches to photoemission [56–62], our ansatz keeps the basic structure of the one-step model, which is highly desirable for means of numerical evaluation [12].

In a preceding study [47] concerning PES and IPE from Ni surfaces, a first pragmatic way to include (non-local) self-energy corrections in the one-step model was presented. That approach, however, was based on some simplifying assumptions by which the emission from different subbands could be treated independently of each other. This has restricted the range of applicability to special regions in \mathbf{k} -space. Furthermore, the method rests on some presuppositions for the pole structure of the self-energy which were shown to be adequate for the case of Ni, but may be too special in other cases. With the present work we also try to overcome these restrictions and aim at an improved concept that allows to include arbitrary self-energy corrections in the one-step model.

The paper is organized as follows: The next section introduces Pendry’s basic formula for the photocurrent. The discussion of the Green function for the initial state in Sec. III elucidates the difficulties that arise within the original formalism for a non-local potential. Sec. IV prepares for the proposed alternative evaluation of Pendry’s formula which is carried out in detail in Sec. V for the initial states, in Sec. VI for the final state, and eventually in Sec. VII where the transition-matrix elements are considered and all partial results are put together. Finally, Sec. VIII concludes our considerations.

II. ONE-STEP MODEL OF PHOTOEMISSION

The starting point for the one-step model of photoemission is Pendry’s formula [12,39]:

$$I^{\text{PES}} \propto f_{\text{F}}(E_1) \text{Im} \langle \epsilon_f \mathbf{k}_{\parallel} \sigma | G_{2\sigma}^+ \Delta G_{1\sigma}^+ \Delta^\dagger G_{2\sigma}^- | \epsilon_f \mathbf{k}_{\parallel} \sigma \rangle. \quad (1)$$

All relevant information on the electronic structure around the Fermi energy and on the one-particle excitations is included in the “low-energy” propagator $G_{1\sigma}^+$, i. e. in the operator representation of the one-electron retarded Green function for the initial state:

$$G_{1\sigma}^+ = \int \int |\mathbf{r}\sigma\rangle G_{\sigma}^+(\mathbf{r}, \mathbf{r}', E_1) \langle \mathbf{r}'\sigma | d\mathbf{r} d\mathbf{r}'. \quad (2)$$

$\sigma = \uparrow, \downarrow$ refers to the z-component of electron spin. E_1 is the initial-state energy, i. e. $E_1 = \epsilon_f - \mu - \hbar\omega$, where ϵ_f denotes the one-particle energy of the outgoing photoelectron, μ stands for the chemical potential, and $\hbar\omega$ is the photon energy. The low-energy propagator $G_{1\sigma}^+$ is directly related to the “bare” photocurrent and thereby represents the central physical quantity within the one-step model.

Referring to an energy-, angle- and spin-resolved photoemission experiment, the state of the photoelectron at the detector is written as $|\epsilon_f \mathbf{k}_{\parallel} \sigma\rangle$, where \mathbf{k}_{\parallel} is the component of the wave vector parallel to the surface. By means of the advanced Green function $G_{2\sigma}^-$ in operator representation and taken at the final-state energy $E_2 \equiv \epsilon_f$, we have $|f\rangle = G_{2\sigma}^- |\epsilon_f \mathbf{k}_{\parallel} \sigma\rangle$ for

the final state in Eq. (1). Furthermore, $\Delta = (e/m_e)\mathbf{A}_0 \cdot \mathbf{p}$ is the dipole operator, i. e. the perturbation which mediates the coupling between the initial and the final state. Δ has been taken in the electric dipole approximation which is well justified in the visible and ultraviolet spectral range. \mathbf{A}_0 is the spatially constant vector potential inside the crystal which can be determined from classical macroscopic dielectric theory.

PES and IPE are complementary spectroscopies. At zero temperature $T = 0$ photoemission probes the occupied and inverse photoemission the unoccupied part of the (quasi-particle) band structure. For PES this fact is accounted for by the Fermi function in Eq. (1): $f_F(E) = 1/(\exp(E/k_B T) + 1)$. Apart from the Fermi function the ratio $I^{\text{PES}}/I^{\text{IPE}}$ is known to depend on kinematic factors only. It is given by the energies and emission angles of the emitted photoelectrons and photons, respectively [14]. We can thus concentrate on PES in the following; IPE may always be treated analogously without any difficulties.

The basic equation (1) for the one-step model of photoemission contains some approximations that should be discussed briefly: First we note that the formula is eventually based on Fermi's golden rule from first-order time-dependent perturbation theory with respect to Δ [39]. This implies that it yields the elastic part of the photocurrent only. So-called vertex renormalizations and three-particle correlation effects are neglected which means the exclusion of inelastic energy losses and corresponding quantum-mechanical interference terms (cf. Refs. [12,61,39]).

The “high-energy” propagator $G_{2\sigma}^-$ is understood to be calculated for a local potential, i. e. assuming $\Sigma_\sigma(\mathbf{r}, \mathbf{r}', E_2) = \delta(\mathbf{r} - \mathbf{r}')\Sigma_\sigma(\mathbf{r}, E_2)$ for the self-energy *at the final state energy* $E = E_2$. This allows us to consider the final state $G_{2\sigma}^-|\epsilon_f \mathbf{k}_\parallel \sigma\rangle$ as a (time-reversed) LEED state as in the conventional one-step model. It can thus be calculated by the standard Korringa-Kohn-Rostocker technique (layer-KKR) [11] (see Sec. VI). Furthermore, the interaction of the outgoing photoelectron with the rest system has been neglected (sudden approximation). This approximation is believed to hold well for not too small photon energies. Let us emphasize that the sudden approximation for the final state is consistent with a local self-energy at $E = E_2$. We assume that many-body effects in the final state $G_{2\sigma}^-|\epsilon_f \mathbf{k}_\parallel \sigma\rangle$ can be sufficiently well accounted for by the inclusion of a spatially constant, complex self-energy correction $\Sigma_f(E_2)$ in the LEED calculation as usual. This weakly energy-dependent self-energy correction has to be distinguished clearly from the (imaginary) optical potential, which phenomenologically takes into account inelastic corrections to the elastic photocurrent [39], and from the (real) inner potential, which serves as a reference energy inside the solid with respect to the vacuum level [63]. The inner potential, the optical potential and the self-energy correction for the final state can formally be included in the definition of a generalized energy-dependent inner potential: $V_{0,2} = V_0(E_2) = V_{0r}(E_2) + iV_{0i}(E_2)$.

While typical values for the final-state energy E_2 may be several tens of eV or even more above the Fermi energy, the energy of the initial state E_1 lies some eV below the Fermi energy. It is this low-energy range that our primary interest should concern since excitations that involve the states in the vicinity of the Fermi energy can be of particular significance for typical electron-correlation effects. These excitations are described by means of the Green function for the initial state $G_{1\sigma}^+$.

III. INITIAL-STATE GREEN FUNCTION

Within the conventional one-step model of Pendry and co-workers [11–13] the initial-state Green function $G_{\mathbf{I}\sigma}^+$ is determined for electrons moving in an (effective) one-particle potential as it is provided, for example, by DFT-LDA:

$$V_{\text{LDA}}(\mathbf{r}, \sigma) = V_{\text{e}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}, \sigma). \quad (3)$$

Within the DFT ground-state formalism the external core potential V_{e} , the Hartree contribution V_{H} as well as the exchange-correlation potential V_{xc} are local functions. On the other hand, it is well known that for an in principle exact description of the one-particle excitations one has to consider the Dyson equation for the Green function [33,64]. This includes the non-local, complex and energy-dependent self-energy. The development of reasonable approximations for the self-energy constitutes a fairly complex many-body problem which falls outside the scope of this paper. Just as the LDA potential, the self-energy must be assumed to be a given quantity for the photoemission theory.

Several techniques that have been developed in the past to account for electron-correlation effects beyond DFT-LDA yield explicit analytical expressions for the self-energy or at least a numerical data set resulting from a self-consistent calculation. Either the self-energy is given in its real-space representation, $\Sigma_{\sigma}(\mathbf{r}, \mathbf{r}', E)$, like in the GW approximation, for example [40–43], or in a tight-binding representation, $\Sigma_{ii'\sigma}^{LL'}(E)$, as it is frequently employed within many-body approaches that consider a degenerate-band Hubbard model with realistic Coulomb-interaction parameters [44–51]. The many-body calculation should explicitly take into account the presence of the solid surface: For PES and IPE the information depth is mainly determined by the electron inelastic mean free path in the solid. Due to the small attenuation length for low-energy electrons [65], PES and IPE are sensitive to a few layers from the surface only. However, all hitherto existing approaches concerning the multi-band Hubbard model refer to an infinitely extended, periodic crystal lattice and benefit from simplifications due to translational symmetry. For the single-band Hubbard model there are recent attempts to take into account the breakdown of translational symmetry at the surface [66–68]. An extension of such real-space many-body techniques to the multi-band case is straightforward.

For the following let us assume that the LDA potential V_{LDA} as well as the self-energy Σ fully account for the presence of the surface. The local LDA potential defines the LDA Hamiltonian:

$$h_{\text{LDA}}(\mathbf{r}, \sigma) = \frac{\mathbf{p}^2}{2m_{\text{e}}} + V_{\text{LDA}}(\mathbf{r}, \sigma). \quad (4)$$

The self-energy is assumed to be defined with respect to h_{LDA} and given in real-space representation for the moment. Therewith, the generalized potential that is obtained by adding the self-energy to the LDA potential,

$$U_{\sigma}(\mathbf{r}, \mathbf{r}', E) = \delta(\mathbf{r} - \mathbf{r}') V_{\text{LDA}}(\mathbf{r}, \sigma) + \Sigma_{\sigma}(\mathbf{r}, \mathbf{r}', E), \quad (5)$$

in principle yields the correct one-particle excitation spectrum. Now the initial-state Green function may be obtained as the solution of the Dyson equation which in real-space representation reads:

$$[E_1 - h_{\text{LDA}}(\mathbf{r}, \sigma)] G_{\sigma}^{+}(\mathbf{r}, \mathbf{r}', E_1) - \int \Sigma_{\sigma}(\mathbf{r}, \mathbf{r}'', E_1) G_{\sigma}^{+}(\mathbf{r}'', \mathbf{r}', E_1) d\mathbf{r}'' = \hbar \delta(\mathbf{r} - \mathbf{r}') . \quad (6)$$

Within the original framework of the one-step model ($\Sigma \equiv 0$) the calculation proceeds by interpreting the Green function as a propagator summing over all scattering paths that take the electron from \mathbf{r}' to \mathbf{r} . Applying the KKR multiple-scattering theory [52–55,11] solves the problem to evaluate the basic formula for the photocurrent (1) very efficiently and has been adopted in the original work [12] as well as (with the necessary modifications) in all subsequent generalizations of the one-step model [16–20,25–27].

A key point of this technique concerns the following expression for the Green function in the presence of a *single* atom with spherically symmetric potential known from scattering theory [69,64,70]:

$$G^{(0)}(\mathbf{r}, \mathbf{r}', E_1) = -i\sqrt{E_1} \sum_{lm} \psi_l(r_{<}) \psi_l^{+}(r_{>}) Y_{lm}(\hat{\mathbf{r}}') Y_{lm}^{*}(\hat{\mathbf{r}}) . \quad (7)$$

Here $r_{<}$, $r_{>}$ stands for the lesser or greater of $|\mathbf{r}|$ and $|\mathbf{r}'|$, $\psi_l(r)$ ($\psi_l^{+}(r)$) is the regular (irregular) solution of the radial Schrödinger equation at energy E_1 , and $Y_{lm}(\hat{\mathbf{r}})$ are the spherical harmonics. The advantage to use the expansion (7) in the basic equation (1) is obvious: One avoids to solve the Dyson equation in the form (6), and the problem separates with respect to the variables \mathbf{r} and \mathbf{r}' . The representation (7) is not restricted to a spherically symmetric potential but can be generalized for potentials of arbitrary shape as has been shown by Butler et al. [70].

However, the proof in (the appendix of) Ref. [70] also shows that a further generalization of (7) to the case of non-local potentials seems to be impossible. Firstly, one surely has to consider $\psi_l(r)$ and $\psi_l^{+}(r)$ as the (radial) solutions of Schrödinger's equation for a non-local (atomic) potential. But even with the correct solutions, the expression (7) does not solve the problem: The reason is that due to the non-locality of the self-energy the cases $r < r'$ and $r > r'$ are mixed and cannot be treated independently in Eq. (6) to show that $[E_1 - h_{\text{LDA}} - \Sigma(E_1)] G^{(0)}(E_1) = 0$ for $r \neq r'$. On the other hand, however, it is necessary to work with $r_{<}$ and $r_{>}$ in (7) in order to get the delta function on the right-hand side of (6) (cf. Ref. [70]). Furthermore, one has to consider multiple-scattering corrections to Eq. (7) when embedding the atom in the crystal lattice. However, there is no generalization of the KKR multiple-scattering formalism to our knowledge that works for a non-local lattice-periodic potential.

Within the original one-step formalism the representation (7) is employed from the very beginning. Consequently, for the case of non-local potentials we have to disregard (7) as well as the multiple-scattering formalism for the calculation of the initial-state Green function $G_{1\sigma}^{+}$ in Pendry's formula.

IV. ALTERNATIVE EVALUATION OF PENDRY'S FORMULA

The alternative is to solve the Dyson equation (6) directly. This, however, requires a revision of the formalism to a large extent. Only for the calculation of the final state the multiple-scattering approach can be retained. In the following it is shown that a consequent reformulation in the sense mentioned is possible indeed.

The Dyson equation is most conveniently solved within a tight-binding representation. For this purpose we choose a set of one-particle wave functions,

$$\Phi_{iL\sigma}(\mathbf{r} - \mathbf{R}_i) \equiv \langle \mathbf{r} | iL\sigma \rangle, \quad (8)$$

which span the subspace \mathcal{H}_S that includes all s-, p-, d- (and f-)like eigenstates of the LDA Hamiltonian h_{LDA} in the vicinity (several eV) of the Fermi energy (minimal basis set):

$$\sum_{ii'LL'} \Phi_{iL\sigma}(\mathbf{r} - \mathbf{R}_i) \left(S_{\sigma}^{-1} \right)_{ii'}^{LL'} \Phi_{i'L'\sigma}^*(\mathbf{r}' - \mathbf{R}_{i'}) = \delta(\mathbf{r} - \mathbf{r}'). \quad (9)$$

The wave functions $\Phi_{iL\sigma}(\mathbf{r} - \mathbf{R}_i)$ are assumed to be well localized at the respective sites \mathbf{R}_i of the crystal lattice. $L = (l, m)$ is a composite index characterizing the electron's angular momentum, and S denotes the overlap matrix:

$$S_{ii'\sigma}^{LL'} = \int \Phi_{iL\sigma}^*(\mathbf{r} - \mathbf{R}_i) \Phi_{i'L'\sigma}(\mathbf{r} - \mathbf{R}_{i'}) d\mathbf{r}. \quad (10)$$

Since the basis functions are chosen to have definite angular-momentum character, the basis is non-orthogonal. Furthermore, the choice of the basis reflects the relevant energy range around the Fermi energy we are interested in. To justify the usual restriction to the subspace \mathcal{H}_S , the states $|iL\sigma\rangle$ are assumed to be orthogonal to all core states at all sites.

Using the tight-binding representation for the LDA Hamiltonian,

$$T_{ii'\sigma}^{LL'} = \langle iL\sigma | h_{\text{LDA}} | i'L'\sigma \rangle \quad (11)$$

and for the self-energy,

$$\Sigma_{ii'\sigma}^{LL'}(E_1) = \langle iL\sigma | \Sigma_{\sigma}(E_1) | i'L'\sigma \rangle, \quad (12)$$

the Dyson equation for the initial-state Green function reads:

$$\sum_{i''L''} \left\{ E_1 S_{ii''\sigma}^{LL''} - T_{ii''\sigma}^{LL''} - \Sigma_{ii''\sigma}^{LL''}(E_1) \right\} G_{i''i'\sigma}^{(+L''L')}(E_1) = \hbar \delta_{ii'} \delta_{LL'}, \quad (13)$$

Within the tight-binding formulation it can be solved numerically by Fourier transformation to \mathbf{k} or \mathbf{k}_{\parallel} space and subsequent matrix inversion. More important, direct contact is made with numerous many-body approaches that likewise refer to a one-particle basis of localized orbitals and yield the self-energy in the form of Eq. (12).

For the evaluation of Pendry's formula we consider the system to be built up from layers parallel to the surface. Because of the damping of the final-state wave field due to the

imaginary part of the inner potential $V_{0i}(E_2)$, it is sufficient to restrict oneself to a finite number of layers, i. e. to a slab geometry. Perfect translational symmetry is assumed within every layer. We label the layers by an index i_\perp . For each we define \mathbf{R}_{i_\perp} to be the position of a reference atom which can be thought of as a local origin for the layer i_\perp . Atoms within the layer i_\perp are labeled by an index i_\parallel . Their positions are given by $\mathbf{R}_i = \mathbf{R}_{i_\parallel} + \mathbf{R}_{i_\perp}$, where \mathbf{R}_{i_\parallel} denotes a vector of the two-dimensional lattice. (For simplicity we consider a system with one atom per layer unit cell.)

Two-dimensional translational symmetry is made explicit in the notation of the basis orbitals:

$$|iL\sigma\rangle \equiv |i_\parallel i_\perp L\sigma\rangle, \quad (14)$$

from which we construct two-dimensional Bloch sums in the following way:

$$|\mathbf{q}_\parallel i_\perp L\sigma\rangle = \frac{1}{\sqrt{N_\parallel}} \sum_{i_\parallel} e^{i\mathbf{q}_\parallel \mathbf{R}_{i_\parallel}} |i_\parallel i_\perp L\sigma\rangle. \quad (15)$$

Here \mathbf{q}_\parallel is a vector of the first Brillouin zone, and N_\parallel denotes the number of atoms within a layer ($N_\parallel \mapsto \infty$). By means of Fourier transformation to the Bloch-sum basis, the Green function can be rewritten as:

$$G_{\mathbf{q}_\parallel i_\perp i_\perp' \sigma}^{(+)LL'}(E_1) = \frac{1}{N_\parallel} \sum_{i_\parallel i_\parallel'} e^{-i\mathbf{q}_\parallel (\mathbf{R}_{i_\parallel} - \mathbf{R}_{i_\parallel'})} G_{ii'\sigma}^{(+)LL'}(E_1). \quad (16)$$

The operator representation of the Green function now reads:

$$G_{1\sigma}^+ = \sum_{\mathbf{q}_\parallel i_\perp i_\perp' LL'} |\mathbf{q}_\parallel i_\perp L\sigma\rangle G_{\mathbf{q}_\parallel i_\perp i_\perp' \sigma}^{(+)LL'}(E_1) \langle \mathbf{q}_\parallel i_\perp' L'\sigma|. \quad (17)$$

The operator $G_{1\sigma}^+$ is independent from the choice of the one-particle basis. Inserting into Pendry's formula, we get:

$$I^{\text{PES}} \propto f_F(E_1) \text{Im} \sum_{i_\perp i_\perp' LL'} \sum_{\mathbf{q}_\parallel} M_{i_\perp L\sigma}(\epsilon_f, \mathbf{k}_\parallel, \mathbf{q}_\parallel) G_{\mathbf{q}_\parallel i_\perp i_\perp' \sigma}^{(+)LL'}(E_1) M_{i_\perp' L'\sigma}^*(\epsilon_f, \mathbf{k}_\parallel, \mathbf{q}_\parallel), \quad (18)$$

where M is the matrix element of the dipole operator between the final state $|f\rangle = G_{2\sigma}^- |\epsilon_f \mathbf{k}_\parallel \sigma\rangle$ and the Bloch sum $|\mathbf{q}_\parallel i_\perp L\sigma\rangle$:

$$M_{i_\perp L\sigma}(\epsilon_f, \mathbf{k}_\parallel, \mathbf{q}_\parallel) = \langle \epsilon_f \mathbf{k}_\parallel \sigma | G_{2\sigma}^+ \Delta | \mathbf{q}_\parallel i_\perp L\sigma \rangle. \quad (19)$$

The final state $G_{2\sigma}^- |\epsilon_f \mathbf{k}_\parallel \sigma\rangle$ is an eigenstate of h_{LDA} with eigenenergy $E_2 = \epsilon_f$. Let us also consider the low-energy eigenstates of h_{LDA} within the subspace \mathcal{H}_S which we refer to in the following as the initial states. These may be characterized by the spin projection σ and the parallel wave vector \mathbf{q}_\parallel which are good quantum numbers:

$$h_{\text{LDA}} |n\mathbf{q}_\parallel \sigma\rangle = \epsilon_{n\sigma}(\mathbf{q}_\parallel) |n\mathbf{q}_\parallel \sigma\rangle. \quad (20)$$

Here $\epsilon_{n\sigma}(\mathbf{q}_{\parallel})$ are the LDA eigenenergies. The LDA eigenstates form an orthonormal basis of \mathcal{H}_S . We make use of them to rewrite the transition-matrix element:

$$M_{i_{\perp}L\sigma}(\epsilon_f, \mathbf{k}_{\parallel}, \mathbf{q}_{\parallel}) = \sum_n \langle \epsilon_f \mathbf{k}_{\parallel} \sigma | G_{2\sigma}^+ \Delta | n \mathbf{q}_{\parallel} \sigma \rangle \langle n \mathbf{q}_{\parallel} \sigma | \mathbf{q}_{\parallel} i_{\perp} L \sigma \rangle. \quad (21)$$

Thereby the matrix element of the dipole operator is given between eigenstates of h_{LDA} . This is shown below (Sec. VII) to facilitate the calculation to a great extent.

We now proceed as follows: In the next section we will deal with the initial states $|n \mathbf{q}_{\parallel} \sigma\rangle$, Sec. VI focusses on the final state $|f\rangle$ until finally we are in the position to derive a computationally feasible expression for the transition-matrix elements in Sec. VII.

V. THE INITIAL STATES

Let us “switch off” the non-local self-energy for a moment, i. e. take $\Sigma \equiv 0$. In this case the Green function becomes diagonal in the orthonormal basis of the initial states:

$$G_{1\sigma}^+ = \sum_{n \mathbf{q}_{\parallel}} |n \mathbf{q}_{\parallel} \sigma\rangle G_{n \mathbf{q}_{\parallel} \sigma}^+(E_1) \langle n \mathbf{q}_{\parallel} \sigma|. \quad (22)$$

We then have

$$-\frac{1}{\pi} \text{Im} G_{n \mathbf{q}_{\parallel} \sigma}^+(E_1) = \hbar \delta(E_1 - (\epsilon_{n\sigma}(\mathbf{q}_{\parallel}) - \mu)) \quad (23)$$

as a factor within Pendry’s formula (1). For the case $\Sigma \equiv 0$ we can thus conclude that it is sufficient to consider merely a single initial state, namely the one with the eigenenergy $\epsilon_{n\sigma}(\mathbf{k}_{\parallel}) = E_1 + \mu = \epsilon_{f\sigma}(\mathbf{k}_{\parallel}) - \hbar\omega$. If the self-energy is switched on again, its imaginary part will cause a broadening of the delta-function indicating a finite quasi-particle lifetime. In a sense the LDA band structure will be smeared out to some degree. Furthermore, strong correlations may lead to satellites in the excitation spectrum which take some spectral weight from the main bands. Both effects imply that for a given photon energy $\hbar\omega$ there may be different initial states $|n \mathbf{q}_{\parallel} \sigma\rangle$ coupled to the same final state $|f\rangle$. Opposed to the conventional evaluation of the one-step model, we thus need all eigenstates of h_{LDA} around the energy $\epsilon_{f\sigma}(\mathbf{k}_{\parallel}) - \hbar\omega$.

We expand the initial states in the Bloch-sum basis:

$$|n \mathbf{q}_{\parallel} \sigma\rangle = \sum_{i_{\perp} L} \alpha_{i_{\perp} L \sigma}^{n \mathbf{q}_{\parallel}} | \mathbf{q}_{\parallel} i_{\perp} L \sigma \rangle. \quad (24)$$

The expansion coefficients $\alpha_{i_{\perp} L \sigma}^{n \mathbf{q}_{\parallel}}$ as well as the LDA eigenenergies have to be determined from the following non-orthogonal eigenvalue problem:

$$\sum_{i_{\perp}' L'} \left(T_{i_{\perp} i_{\perp}' \sigma}^{LL'}(\mathbf{q}_{\parallel}) - \epsilon_{n\sigma}(\mathbf{q}_{\parallel}) S_{i_{\perp} i_{\perp}' \sigma}^{LL'}(\mathbf{q}_{\parallel}) \right) \alpha_{i_{\perp}' L' \sigma}^{n \mathbf{q}_{\parallel}} = 0, \quad (25)$$

which is easily derived from (20) when expressing the LDA-Hamiltonian and the overlap within the Bloch-sum basis:

$$\begin{aligned} T_{i_{\perp}i_{\perp}'}^{LL'}(\mathbf{q}_{\parallel}) &= \langle \mathbf{q}_{\parallel} i_{\perp} L \sigma | h_{\text{LDA}} | \mathbf{q}_{\parallel} i_{\perp}' L' \sigma \rangle, \\ S_{i_{\perp}i_{\perp}'}^{LL'}(\mathbf{q}_{\parallel}) &= \langle \mathbf{q}_{\parallel} i_{\perp} L \sigma | \mathbf{q}_{\parallel} i_{\perp}' L' \sigma \rangle. \end{aligned} \quad (26)$$

The \mathbf{q}_{\parallel} -dependent (LDA-)Hamilton and overlap matrices are connected with the Hamilton and overlap matrices from Eqs. (10) and (11) via two-dimensional Fourier transformation:

$$\begin{aligned} T_{ii'\sigma}^{LL'} &= \frac{1}{N_{\parallel}} \sum_{\mathbf{q}_{\parallel}} e^{i\mathbf{q}_{\parallel}(\mathbf{R}_{i_{\parallel}} - \mathbf{R}_{i'_{\parallel}})} T_{i_{\perp}i_{\perp}'}^{LL'}(\mathbf{q}_{\parallel}), \\ S_{ii'\sigma}^{LL'} &= \frac{1}{N_{\parallel}} \sum_{\mathbf{q}_{\parallel}} e^{i\mathbf{q}_{\parallel}(\mathbf{R}_{i_{\parallel}} - \mathbf{R}_{i'_{\parallel}})} S_{i_{\perp}i_{\perp}'}^{LL'}(\mathbf{q}_{\parallel}). \end{aligned} \quad (27)$$

From Eqs. (24) and (26) we have:

$$\langle n\mathbf{q}_{\parallel}\sigma | \mathbf{q}_{\parallel} i_{\perp} L \sigma \rangle = \sum_{i_{\perp}'L'} \left(\alpha_{i_{\perp}'L'\sigma}^{n\mathbf{q}_{\parallel}} \right)^* S_{i_{\perp}'i_{\perp}\sigma}^{L'L}(\mathbf{q}_{\parallel}), \quad (28)$$

which gives us the second factor in Eq. (21) for the transition-matrix elements.

For the first factor, i. e. for the actual matrix element, we need the real-space representation of the initial state $|n\mathbf{q}_{\parallel}\sigma\rangle$:

$$\Psi_{\mathbf{q}_{\parallel}\sigma}^{(n)}(\mathbf{r}) \equiv \langle \mathbf{r} | n\mathbf{q}_{\parallel}\sigma \rangle = \sum_{i_{\perp}L} \alpha_{i_{\perp}L\sigma}^{n\mathbf{q}_{\parallel}} \Phi_{i_{\perp}L\sigma}^{\mathbf{q}_{\parallel}}(\mathbf{r} - \mathbf{R}_{i_{\perp}}). \quad (29)$$

Here we have introduced the real-space representation of the Bloch sums [cf. Eqs. (8) and (15)]:

$$\Phi_{i_{\perp}L\sigma}^{\mathbf{q}_{\parallel}}(\mathbf{r} - \mathbf{R}_{i_{\perp}}) \equiv \langle \mathbf{r} | \mathbf{q}_{\parallel} i_{\perp} L \sigma \rangle = \frac{1}{\sqrt{N_{\parallel}}} \sum_{i_{\parallel}} e^{i\mathbf{q}_{\parallel}\mathbf{R}_{i_{\parallel}}} \Phi_{i_{\parallel}L\sigma}(\mathbf{r} - \mathbf{R}_i). \quad (30)$$

To proceed further, it becomes necessary to specify the basis orbitals $\Phi_{iL\sigma}(\mathbf{r})$ and the form of the LDA potential. We assume that $V_{\text{LDA}}(\mathbf{r})$ can be sufficiently well approximated by a muffin-tin potential, which is spherically symmetric within non-overlapping muffin-tin spheres centered at the lattice sites \mathbf{R}_i and constant inbetween. The muffin-tin approximation will greatly facilitate the calculation of the transition-matrix elements since we then have a simple separation in radial and angular parts. This also implies the need for a one-center expansion of the initial states (29) and thus of the Bloch sums, which in Eq. (30) are given in terms of the basis orbitals centered at all sites i_{\parallel} within a layer i_{\perp} . For this purpose we may choose the basis orbitals to be (augmented) muffin-tin orbitals (MTO's) [71,72]. Being orthogonal to all core states at all sites of the lattice and spanning the subspace $\mathcal{H}_{\mathcal{S}}$, they have all the properties we demanded above. Furthermore, we have the desired one-center expansion for the Bloch sum of the MTO's of a layer i_{\perp} :

$$\sqrt{N_{\parallel}} \Phi_{i_{\perp}L\sigma}^{\mathbf{q}_{\parallel}}(\mathbf{r} - \mathbf{R}_{i_{\perp}}) = \delta_{i_{\perp}'i_{\perp}} \Phi_{i_{\perp}L\sigma}(\mathbf{r} - \mathbf{R}_{i_{\perp}'}) - \sum_{L'} Z_{L'L}^{i_{\perp}'i_{\perp}}(\mathbf{q}_{\parallel}) \tilde{\Phi}_{i_{\perp}'L'\sigma}(\mathbf{r} - \mathbf{R}_{i_{\perp}'}). \quad (31)$$

The expansion converges within the muffin-tin sphere at $\mathbf{R}_{i_{\parallel}'} = 0$ of a given layer i_{\perp}' [71]. Z is the potential-independent structure constant and $\tilde{\Phi}$ an augmented spherical Bessel

function. Let us mention that the existence of the one-center expansion rests on an analogous expansion theorem for the spherical Neumann functions and not necessarily on the muffin-tin form of the LDA potential [72]. Φ and $\tilde{\Phi}$ are separated into a radial and an angular part:

$$\begin{aligned}\Phi_{iL\sigma}(\mathbf{r}) &= \phi_{iL\sigma}(r)Y_L(\hat{\mathbf{r}}), \\ \tilde{\Phi}_{iL\sigma}(\mathbf{r}) &= \tilde{\phi}_{iL\sigma}(r)Y_L(\hat{\mathbf{r}}).\end{aligned}\tag{32}$$

Because of two-dimensional translational symmetry within a layer, the radial parts are the same for all sites i_{\parallel} within a layer and depend on the layer index i_{\perp} only. A further specification of the radial parts is not necessary for our present purposes.

Inserting (31) and (32) into (29) we get

$$\Psi_{\mathbf{q}_{\parallel}\sigma}^{(n)}(\mathbf{r}) = \frac{1}{\sqrt{N_{\parallel}}} \sum_L \left[B_{i_{\perp}L\sigma}^{n\mathbf{q}_{\parallel}} \phi_{i_{\perp}L\sigma}(|\mathbf{r} - \mathbf{R}_{i_{\perp}}|) + \tilde{B}_{i_{\perp}L\sigma}^{n\mathbf{q}_{\parallel}} \tilde{\phi}_{i_{\perp}L\sigma}(|\mathbf{r} - \mathbf{R}_{i_{\perp}}|) \right] Y_L(\widehat{\mathbf{r} - \mathbf{R}_{i_{\perp}}}), \tag{33}$$

where we have defined

$$\begin{aligned}B_{i_{\perp}L\sigma}^{n\mathbf{q}_{\parallel}} &= \alpha_{i_{\perp}L\sigma}^{n\mathbf{q}_{\parallel}}, \\ \tilde{B}_{i_{\perp}L\sigma}^{n\mathbf{q}_{\parallel}} &= \sum_{i_{\perp}'L'} Z_{LL'}^{i_{\perp}i_{\perp}'}(\mathbf{q}_{\parallel}) \alpha_{i_{\perp}'L'\sigma}^{n\mathbf{q}_{\parallel}}.\end{aligned}\tag{34}$$

Therewith we have the final one-center expansion of the initial states into spherical harmonics.

VI. THE FINAL STATE

For the determination of the final state

$$\Psi_{\mathbf{k}_{\parallel}\sigma}^{(f)}(\mathbf{r}) = \langle \mathbf{r} | G_{2\sigma}^- | \epsilon_f \mathbf{k}_{\parallel} \sigma \rangle \tag{35}$$

we consider a conventional diffraction situation with $|\epsilon_f \mathbf{k}_{\parallel} \sigma\rangle$ (the state in the vacuum at the photoelectron detector) interpreted as a *source* of electrons which penetrate into the crystal. Within the framework of the layer-KKR multiple-scattering formalism [52–55,11] we can construct the whole high-energy wave field from the source $|\epsilon_f \mathbf{k}_{\parallel} \sigma\rangle$ and from the scattering properties of each layer. The result gives us the *time-reversed* final state $\left(\Psi_{\mathbf{k}_{\parallel}\sigma}^{(f)}(\mathbf{r})\right)^*$. Just as in the case of the initial states the main goal is to derive a one-center expansion of the final state into spherical harmonics within a given muffin-tin sphere at $\mathbf{r} = \mathbf{R}_{i_{\parallel}} + \mathbf{R}_{i_{\perp}}$.

To begin with, we consider the region of constant inner potential $V_{0,2}$ between the muffin-tin spheres where plane waves are solutions of Schrödinger's equation. The potential V_{LDA} can be assumed to be invariant under two-dimensional lattice translations $\mathbf{r} \mapsto \mathbf{r} + \mathbf{R}_{i_{\parallel}}$. For any multiple-scattering event this implies that the wave vector parallel to the surface \mathbf{k}_{\parallel} can be changed by a reciprocal lattice vector \mathbf{g}_{\parallel} only. In the interstitial region the high-energy wave field can thus be expanded into plane waves with wave vectors

$$\mathbf{k}_{\mathbf{g}_{\parallel}}^{\pm} = \left(-\mathbf{k}_{\parallel} + \mathbf{g}_{\parallel}, \pm \sqrt{2m_e(E_2 - V_{0,2})/\hbar^2 - |\mathbf{k}_{\parallel} + \mathbf{g}_{\parallel}|^2} \right). \quad (36)$$

We define the positive z -axis pointing into the crystal and choose $\mathbf{r} = \mathbf{R}_{i_{\perp}}$ to be a local origin for a given layer i_{\perp} . Consider then a plane-wave field advancing on the layer from the $+z$ side:

$$\frac{1}{\sqrt{N_{\parallel}}} \sum_{\mathbf{g}_{\parallel}} W_{\mathbf{g}_{\parallel} i_{\perp} \sigma}^{+} e^{i\mathbf{k}_{\mathbf{g}_{\parallel}}^{+}(\mathbf{r} - \mathbf{R}_{i_{\perp}})}. \quad (37)$$

Scattering at the layer i_{\perp} gives rise to a transmitted and to a reflected wave field on the $+z$ and the $-z$ side of the layer with coefficients $V_{\mathbf{g}_{\parallel} i_{\perp} \sigma}^{+}$ and $W_{\mathbf{g}_{\parallel} i_{\perp} \sigma}^{-}$, respectively. They are given via the transmission and reflection matrices:

$$\begin{aligned} V_{\mathbf{g}_{\parallel} i_{\perp} \sigma}^{+} &= \sum_{\mathbf{g}'_{\parallel}} T_{\mathbf{g}_{\parallel} \mathbf{g}'_{\parallel}}^{i_{\perp} \sigma} W_{\mathbf{g}'_{\parallel} i_{\perp} \sigma}^{+}, \\ W_{\mathbf{g}_{\parallel} i_{\perp} \sigma}^{-} &= \sum_{\mathbf{g}'_{\parallel}} R_{\mathbf{g}_{\parallel} \mathbf{g}'_{\parallel}}^{i_{\perp} \sigma} W_{\mathbf{g}'_{\parallel} i_{\perp} \sigma}^{+}. \end{aligned} \quad (38)$$

Similar relations hold for an advancing wave field from the $-z$ side. Conventional LEED theory [11] provides us with explicit expressions for the scattering matrices, let us cite the final result:

$$\begin{aligned} T_{\mathbf{g}_{\parallel} \mathbf{g}'_{\parallel}}^{i_{\perp} \sigma} &= \frac{8\pi^2}{\kappa A |k_{\mathbf{g}_{\parallel} z}^{+}|} \sum_{LL'} i^{-l} Y_L(\widehat{\mathbf{k}_{\mathbf{g}'_{\parallel}}^{+}}) t_{li_{\perp} \sigma} (\mathbf{1} - \mathbf{X})_{LL'}^{-1} i^{l'} (-1)^{m'} Y_{\overline{L'}}(\widehat{\mathbf{k}_{\mathbf{g}_{\parallel}}^{+}}) + \delta_{\mathbf{g}_{\parallel} \mathbf{g}'_{\parallel}}, \\ R_{\mathbf{g}_{\parallel} \mathbf{g}'_{\parallel}}^{i_{\perp} \sigma} &= \frac{8\pi^2}{\kappa A |k_{\mathbf{g}_{\parallel} z}^{+}|} \sum_{LL'} i^{-l} Y_L(\widehat{\mathbf{k}_{\mathbf{g}'_{\parallel}}^{+}}) t_{li_{\perp} \sigma} (\mathbf{1} - \mathbf{X})_{LL'}^{-1} i^{l'} (-1)^{m'} Y_{\overline{L'}}(\widehat{\mathbf{k}_{\mathbf{g}_{\parallel}}^{+}}). \end{aligned} \quad (39)$$

Here we have written $t_{li_{\perp} \sigma} = (e^{2i\delta_{li_{\perp} \sigma}} - 1)/2$ for abbreviation. By $\delta_{li_{\perp} \sigma}$ we denote the layer- and spin-dependent phase shifts which completely characterize the scattering properties of the spherically symmetric potential within a single muffin-tin sphere. Furthermore, A stands for the area of the layer unit cell, $\kappa = \sqrt{2m_e(E_2 - V_{0,2})/\hbar}$ and $\overline{L} = (l, -m)$. The matrix

$$X_{LL'} = t_{li_{\perp} \sigma} \sum_{i_{\parallel} L''}' 4\pi i^{(l-l'-l'')} h_{l''}^{(1)}(-\mathbf{k}_{\parallel} \mathbf{R}_{i_{\parallel}}) Y_{\overline{L''}}(-\widehat{\mathbf{R}_{i_{\parallel}}}) (-1)^{(m'+m'')} C_{\overline{L} \overline{L'} L''} e^{i\mathbf{k}_{\parallel} \mathbf{R}_{i_{\parallel}}}, \quad (40)$$

which is due to Kambe [54,55], corrects for intra-layer multiple-scattering events. Here $h_l^{(1)}$ denotes the spherical Hankel function and

$$C_{LL'L''} = \int_{(4\pi)} Y_L(\Omega) Y_{L'}(\Omega) Y_{L''}(\Omega) d\Omega \quad (41)$$

are the Gaunt coefficients. The definition of the X -matrix is closely related to the structure constants defined via Eq. (31) [71].

By the matrices (39) the scattering properties of all layers are known. For a given plane wave $|\epsilon_f \mathbf{k}_{\parallel} \sigma\rangle$ advancing onto the crystal from the vacuum side, they determine the whole high-energy wave field between all layers in the semi-infinite crystal. Its coefficients can

straightforwardly be found within a recursive layer-by-layer scheme [12]. Since the flux of elastically scattered electrons is permanently reduced due to the imaginary part of the (generalized) inner potential, the wave field can be neglected beyond a finite depth.

Once all coefficients of the plane-wave expansions are known, the next step will be to derive an expansion of the high-energy wave field into spherical harmonics centered at the local origin $\mathbf{R}_{i\perp}$ of a layer $i\perp$. The advancing plane-wave field at the layer $i\perp$ is:

$$\Psi_{\mathbf{k}_{\parallel}i\perp\sigma}^{(0)}(\mathbf{r}) = \frac{1}{\sqrt{N_{\parallel}}} \sum_{\mathbf{g}_{\parallel}} \left(W_{\mathbf{g}_{\parallel}i\perp\sigma}^{+} e^{i\mathbf{k}_{\mathbf{g}_{\parallel}}^{+}(\mathbf{r}-\mathbf{R}_{i\perp})} + V_{\mathbf{g}_{\parallel}i\perp\sigma}^{-} e^{i\mathbf{k}_{\mathbf{g}_{\parallel}}^{-}(\mathbf{r}-\mathbf{R}_{i\perp})} \right), \quad (42)$$

where $W_{\mathbf{g}_{\parallel}i\perp\sigma}^{+}$ and $V_{\mathbf{g}_{\parallel}i\perp\sigma}^{-}$ are the coefficients of the plane waves on the $-z$ and the $+z$ side of the layer, respectively. From (42) we get the spherical wave amplitudes

$$A_{i\perp L\sigma}^{\mathbf{k}_{\parallel}(0)} = \frac{1}{\sqrt{N_{\parallel}}} \sum_{\mathbf{g}_{\parallel}} 4\pi i^l (-1)^m \left(W_{\mathbf{g}_{\parallel}i\perp\sigma}^{+} Y_L^{-}(\widehat{\mathbf{k}_{\mathbf{g}_{\parallel}}^{+}}) + V_{\mathbf{g}_{\parallel}i\perp\sigma}^{-} Y_L^{-}(\widehat{\mathbf{k}_{\mathbf{g}_{\parallel}}^{-}}) \right) \quad (43)$$

of the advancing wave field:

$$\Psi_{\mathbf{k}_{\parallel}i\perp\sigma}^{(0)}(\mathbf{R}_{i\perp} + \mathbf{r}) = \sum_L A_{i\perp L\sigma}^{\mathbf{k}_{\parallel}(0)} j_l(\kappa r) Y_L(\Omega), \quad (44)$$

where j_l is the spherical Bessel function. Correcting for multiple scattering within the layer [12],

$$A_{i\perp L\sigma}^{\mathbf{k}_{\parallel}} = \sum_{L'} A_{i\perp L'\sigma}^{\mathbf{k}_{\parallel}(0)} (\mathbf{1} - \mathbf{X})_{L'L}^{-1}, \quad (45)$$

we arrive at the total final-state wave field inside the muffin-tin sphere at $\mathbf{R}_{i\perp}$:

$$\left(\Psi_{\mathbf{k}_{\parallel}\sigma}^{(f)}(\mathbf{r}) \right)^* = \frac{1}{\sqrt{N_{\parallel}}} \sum_L A_{i\perp L\sigma}^{\mathbf{k}_{\parallel}} e^{i\delta_{li\perp\sigma}} \psi_{i\perp l\sigma}(|\mathbf{r} - \mathbf{R}_{i\perp}|) Y_L(\widehat{\mathbf{r} - \mathbf{R}_{i\perp}}). \quad (46)$$

$\psi_{i\perp l\sigma}(r)$ is the radial part of the solution of the Schrödinger equation for energy E_2 that is regular at the origin. The radial function as well as the phase shifts have to be determined numerically for the spherically symmetric LDA potential within the muffin-tin sphere at $\mathbf{R}_{i\perp}$.

VII. THE TRANSITION-MATRIX ELEMENTS

We are now in a position that allows for calculating the actual transition-matrix elements, i. e. the first factor in Eq. (21). Again we turn to real-space representation:

$$\langle \epsilon_f \mathbf{k}_{\parallel} \sigma | G_{2\sigma}^{+} \Delta | n \mathbf{q}_{\parallel} \sigma \rangle = \frac{-i\hbar e}{m_e} \int \left(\Psi_{\mathbf{k}_{\parallel}\sigma}^{(f)}(\mathbf{r}) \right)^* (\mathbf{A}_0 \nabla) \Psi_{\mathbf{q}_{\parallel}\sigma}^{(n)}(\mathbf{r}) d\mathbf{r}. \quad (47)$$

Since $[\nabla, h_{\text{LDA}}]_{-} = \nabla V_{\text{LDA},\sigma}(\mathbf{r})$, the transition-matrix element can be rewritten as:

$$\langle \epsilon_f \mathbf{k}_{\parallel} \sigma | G_{2\sigma}^+ \Delta | n \mathbf{q}_{\parallel} \sigma \rangle = \frac{i\hbar e}{m_e} \frac{1}{\epsilon_{f\sigma}(\mathbf{k}_{\parallel}) - \epsilon_{n\sigma}(\mathbf{q}_{\parallel})} \int (\Psi_{\mathbf{k}_{\parallel}\sigma}^{(f)}(\mathbf{r}))^* (\mathbf{A}_0 \nabla V_{\text{LDA},\sigma}(\mathbf{r})) \Psi_{\mathbf{q}_{\parallel}\sigma}^{(n)}(\mathbf{r}) d\mathbf{r}. \quad (48)$$

Here we made use of the fact that both, the final state $\Psi^{(f)}$ and the initial states $\Psi^{(n)}$, are eigenstates of h_{LDA} . At this point we thus profit from the transformation of the transition-matrix element (19) into the expression given by Eq. (21). Since $\nabla V_{\text{LDA},\sigma}(\mathbf{r}) \equiv 0$ in the region of constant inner potential between the muffin-tin spheres, the integral in (48) now reduces to a sum of integrals over all muffin-tin spheres:

$$\begin{aligned} \nabla V_{\text{LDA},\sigma}(\mathbf{r}) &= \sum_i \Theta_{\text{MT}}(\mathbf{r} - \mathbf{R}_i) \nabla V_{\text{LDA},\sigma}(\mathbf{r}) \\ &\equiv \sum_i \nabla V_{i\sigma}(\mathbf{r} - \mathbf{R}_i), \end{aligned} \quad (49)$$

where $\Theta_{\text{MT}}(\mathbf{r}) = 1$ for $r < r_{\text{MT}}$ and $\Theta_{\text{MT}}(\mathbf{r}) = 0$ for $r > r_{\text{MT}}$, and r_{MT} is the radius of the muffin-tin sphere. $V_{i\sigma}(\mathbf{r}) = V_{i\sigma}(r)$ is the potential within the sphere at the site i with $V_{i\sigma}(r) = 0$ for $r > r_{\text{MT}}$.

Another considerable simplification of the transition-matrix elements arises from the two-dimensional lattice periodicity of the LDA potential, $V_{i\sigma} = V_{i_{\perp}\sigma}$: Since both, the final state and the initial states, fulfill the two-dimensional analogue of Bloch's theorem, any lattice translation of the form $\mathbf{r} \mapsto \mathbf{r} + \mathbf{R}_{i_{\parallel}}$ leaves the integral (48) invariant apart from a factor $\exp(i(\mathbf{q}_{\parallel} - \mathbf{k}_{\parallel})\mathbf{R}_{i_{\parallel}})$. We thus can conclude that the difference $\mathbf{q}_{\parallel} - \mathbf{k}_{\parallel}$ is equal to a reciprocal lattice vector \mathbf{g}_{\parallel} . Since we can consider \mathbf{k}_{\parallel} to be fixed by the energy of the photoelectron at the detector and by the emission angles, the reciprocal lattice vector is uniquely determined by demanding \mathbf{q}_{\parallel} to lie within the first surface Brillouin zone. Hence, translational symmetry reduces the \mathbf{q}_{\parallel} -sum in Eq. (18) to a single term:

$$\mathbf{q}_{\parallel} = \mathbf{k}_{\parallel} + \mathbf{g}_{\parallel}. \quad (50)$$

Referring once more to translational symmetry, we also conclude that all integrals over muffin-tin spheres within the same layer i_{\perp} are equal. This leads us finally to:

$$\begin{aligned} \langle \epsilon_f \mathbf{k}_{\parallel} \sigma | G_{2\sigma}^+ \Delta | n(\mathbf{k}_{\parallel} + \mathbf{g}_{\parallel}) \sigma \rangle &= \\ N_{\parallel} \frac{i\hbar e}{m_e} \frac{1}{\epsilon_{f\sigma}(\mathbf{k}_{\parallel}) - \epsilon_{n\sigma}(\mathbf{k}_{\parallel} + \mathbf{g}_{\parallel})} \int_{S(i_{\perp})} (\Psi_{\mathbf{k}_{\parallel}\sigma}^{(f)}(\mathbf{r}))^* \mathbf{A}_0 \nabla V_{i_{\perp}\sigma}(\mathbf{r} - \mathbf{R}_{i_{\perp}}) \Psi_{\mathbf{k}_{\parallel} + \mathbf{g}_{\parallel}\sigma}^{(n)}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (51)$$

where the integral extends over the sphere at the local origin $\mathbf{R}_{i_{\perp}}$ of the layer i_{\perp} .

For the evaluation of the integral we separate into radial and angular parts. For this purpose we need the expansion of the dipole operator into spherical harmonics:

$$\begin{aligned} \mathbf{A}_0 \nabla V_{i_{\perp}\sigma}(r) &= \frac{dV_{i_{\perp}\sigma}(r)}{dr} A_0 \frac{\mathbf{A}_0 \mathbf{r}}{A_0 r} \\ &= \frac{dV_{i_{\perp}\sigma}(r)}{dr} A_0 \frac{4\pi}{3} \sum_{m=-1}^1 Y_{1m}^*(\widehat{\mathbf{A}_0}) Y_{1m}(\hat{\mathbf{r}}) \end{aligned} \quad (52)$$

and the one-center expansions of the initial states (33) and the final state (46) as derived in Secs. V and VI. The integration over the angular parts can be performed analytically and yields the following angular matrix elements:

$$D_{LL'} = \frac{4\pi}{3} A_0 Y_{1m}^* (\widehat{\mathbf{A}_0}) C_{lm'l'm'1(-m-m')} , \quad (53)$$

where we have used the definition (41) of the Gaunt coefficients. The integration over the radial parts results in two types of radial matrix elements:

$$\begin{aligned} M_{i_\perp l' \sigma} &= e^{i\delta_{l i_\perp \sigma}} \int_0^{r_{\text{MT}}} r^2 \psi_{i_\perp l \sigma}(r) \frac{dV_{i_\perp \sigma}}{dr}(r) \phi_{i_\perp l' \sigma}(r) dr , \\ \widetilde{M}_{i_\perp l' \sigma} &= e^{i\delta_{l i_\perp \sigma}} \int_0^{r_{\text{MT}}} r^2 \psi_{i_\perp l \sigma}(r) \frac{dV_{i_\perp \sigma}}{dr}(r) \widetilde{\phi}_{i_\perp l' \sigma}(r) dr , \end{aligned} \quad (54)$$

in the definition of which we included the phase shifts from Eq. (46). Since $\psi_{i_\perp l \sigma}(r)$ as well as $\phi_{i_\perp l \sigma}(r)$ and $\widetilde{\phi}_{i_\perp l \sigma}(r)$ are regular functions at $r = 0$ and since $V_{i_\perp \sigma}(r) \propto -Z/r$ for $r \mapsto 0$, the integrals are well defined.

The final formula for the photocurrent now reads:

$$I^{\text{PES}} \propto f_{\text{F}}(E_1) \text{Im} \sum_{i_\perp i_\perp'} \sum_{LL'} M_{i_\perp L \sigma}(\epsilon_f, \mathbf{k}_\parallel) G_{\mathbf{k}_\parallel + \mathbf{g}_\parallel, i_\perp i_\perp' \sigma}^{(+)\text{LL}'}(E_1) M_{i_\perp' L' \sigma}^*(\epsilon_f, \mathbf{k}_\parallel) , \quad (55)$$

where

$$\begin{aligned} M_{i_\perp L \sigma}(\epsilon_f, \mathbf{k}_\parallel) &= \frac{ie\hbar}{m_e} \sum_n \frac{1}{\epsilon_{f\sigma}(\mathbf{k}_\parallel) - \epsilon_{n\sigma}(\mathbf{k}_\parallel + \mathbf{g}_\parallel)} \times \\ &\quad \left(\sum_{i_\perp' L'} \left(\alpha_{i_\perp' L' \sigma}^{n\mathbf{k}_\parallel + \mathbf{g}_\parallel} \right)^* S_{i_\perp' i_\perp \sigma}^{L' L}(\mathbf{k}_\parallel + \mathbf{g}_\parallel) \right) \times \\ &\quad \left(\sum_{i_\perp' LL'} D_{LL'} A_{i_\perp' L \sigma}^{\mathbf{k}_\parallel} \left(M_{i_\perp' l' \sigma} B_{i_\perp' L' \sigma}^{n\mathbf{k}_\parallel + \mathbf{g}_\parallel} + \widetilde{M}_{i_\perp' l' \sigma} \widetilde{B}_{i_\perp' L' \sigma}^{n\mathbf{k}_\parallel + \mathbf{g}_\parallel} \right) \right) . \end{aligned} \quad (56)$$

This completes the formalism. Combining the essentials of the previous sections, Eqs. (55) and (56) express the result in a rather compact form.

VIII. CONCLUDING REMARKS

This paper has proposed a theory of photoemission (and inverse photoemission) from single-crystal surfaces that keeps the basic structure of the well-known one-step model but determines the initial-state Green function from the Dyson equation rather than by means of KKR multiple-scattering theory. This approach requires to reconsider the calculation of the transition-matrix elements which has been worked out in detail.

In our opinion it is an important advantage of the presented reformulation that the main physical concepts inherent in the one-step model show up in a very transparent way:

- i) The structure of the final equation (55) for the photocurrent is still reminiscent of first-order perturbation theory in the external electric field (Fermi's golden rule).
- ii) Consequently, one can easily distinguish between the “bare” spectrum which essentially is given by the Green function on the one hand and its modifications due to secondary

effects arising from the wave-vector and energy dependence of the transition-matrix elements on the other.

iii) Due to the Fermi-function cut off (for $T = 0$), a non-zero intensity is found for energies $E_1 < 0$ only, i. e. for $\epsilon_f - \hbar\omega < \mu$: The initial-state Green function in (55) describes *hole* propagation, namely propagation of the residual hole in the valence band that corresponds to the excited photoelectron. Since we applied the sudden approximation, photoelectron and hole propagate independently from each other in time. However, energy conservation is satisfied, and thus the photoelectron takes away the information on the hole-excitation spectrum. The energy dependence of the photoemission spectrum originates from the energy dependence of the initial-state (hole) Green function and is shifted by the photon energy $\hbar\omega$.

iv) The theory is able to account for electron-correlation effects *in the initial state*; in (55) $G_{1\sigma}^+$ is the *fully interacting* Green function. Final-state correlation effects (beyond LDA) are included only phenomenologically via the generalized inner potential $V_{0,2}$.

v) The two-dimensional translational invariance of the surface is obvious in the notations. The Green function and the matrix elements are diagonal with respect to $\mathbf{q}_{\parallel} = \mathbf{k}_{\parallel} + \mathbf{g}_{\parallel}$; the same holds for spin projection σ . On the contrary, the problem does not separate with respect to layer and angular-momentum indices. However, the result allows to distinguish between the different partial contributions corresponding to hole propagation from (i_{\perp}, L) to (i'_{\perp}, L') .

Apart from the advantage mentioned above, the main goal of the present study has been to overcome the restriction to local potentials which is inherent in the original formulation of the one-step model. This is a necessary precondition to be able to benefit from many-body theories which in general yield non-local self-energy corrections to the local LDA potential. Up to now these could not be used in the one-step model since they are incompatible with the KKR formalism for the initial state. If, on the contrary, the Dyson equation for the Green function in a muffin-tin-orbitals representation is chosen as the starting point, an unproblematic connection to the results of many-body electronic-structure calculations is possible. Photoemission calculations based on this new concept are intended for the future.

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